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# Copper(I) Cyanide Networks with 1-Phenylpiperazine

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## Abstract:

Aqueous reactions of copper(I) cyanide with 1-phenylpiperazine (PhPip) in the presence of KCN produce network compounds having CuCN:PhPip stoichiometries of 1:1, 3:2, and 4:1 depending on the mixing ratio used. In addition to these phases, hydrothermal synthesis yields a 5:3 network. Crystal structures of these four compounds are reported herein. The (CuCN)(PhPip) network (**1**) forms sheets consisting of Cu centers that coordinate all PhPip via N<sub>H</sub> only, and are linked together by  $\mu_3$ -cyano bridges. The (CuCN)<sub>3</sub>(PhPip)<sub>2</sub> network (**2**) exists as a series of dual-chain ladders. All Cu centers are 3-coordinate and half of the PhPip ligands bridge pairs of chains using both N<sub>H</sub> and N<sub>Ph</sub>, while the other PhPip are only N<sub>H</sub> bound. The (CuCN)<sub>5</sub>(PhPip)<sub>3</sub> network (**3**) forms three independent sets of 1D chains: 2[(CuCN)(PhPip)]•(CuCN)<sub>3</sub>(PhPip). Both 2- and 3-coordinate copper atoms are present and all PhPip ligands bond only through N<sub>H</sub>. The (CuCN)<sub>4</sub>(PhPip) network (**4**) forms identical, but orthogonal, interpenetrating sheets consisting of 2- and 3-coordinate CuCN chains linked by bridging PhPip ligands. Pairwise cuprophilic interactions are seen in the 5:3 and 4:1 networks. The 3:2 compound shows visible photoluminescence associated with Cu-CN MLCT. Compound **1** crystallizes in the monoclinic  $P2_1/c$  space group with cell parameters:  $a = 17.6123(3) \text{ \AA}$ ,  $b = 6.89480(10) \text{ \AA}$ ,  $c = 8.6154(2) \text{ \AA}$ ,  $\beta = 96.1460(10)$ ,  $V = 1040.18(3) \text{ \AA}^3$ , and  $Z = 4$ . Compound **2** crystallizes in the triclinic  $P\bar{1}$  space group with cell parameters:  $a = 9.93710(10) \text{ \AA}$ ,  $b = 10.6359(2) \text{ \AA}$ ,  $c = 12.1230(2) \text{ \AA}$ ,  $\alpha = 105.7110(10)$ ,  $\beta = 100.6110(10)$ ,  $\gamma = 97.7230(10)$ ,  $V = 1189.11(3) \text{ \AA}^3$ , and  $Z = 2$ . Compound **3** crystallizes in the monoclinic  $P2_1/n$  space group with cell parameters:  $a = 15.9018(2) \text{ \AA}$ ,  $b = 9.38850(10) \text{ \AA}$ ,  $c = 26.1864(3) \text{ \AA}$ ,  $\beta = 104.5110(10)$ ,  $V = 3784.76(8) \text{ \AA}^3$ , and  $Z = 4$ . Compound **4** crystallizes in the monoclinic  $P2_1$  space group with cell parameters:  $a = 13.4773(3) \text{ \AA}$ ,  $b = 7.8460(2) \text{ \AA}$ ,  $c = 8.5527(2) \text{ \AA}$ ,  $\beta = 105.1820(10)$ ,  $V = 872.82(4) \text{ \AA}^3$ , and  $Z = 2$ .

## Introduction:

Copper(I) salts have been found to be excellent network-formers. Although Cu(I) is often regarded as too unstable to make robust complexes, its redox stability is greatly enhanced by the use of soft anions, such as iodide, cyanide or thiocyanate. In addition, these inner sphere anions tend to bridge the metal centers, increasing the degree of networking and greatly lessening the tendency of Cu(I) to undergo ligand substitution. We and others have recently reported a wide array of network complexes based on CuCN [1]–[3] and CuSCN [4],[5] using bridging diamine or sulfide ligands. Multiple stoichiometries and polymorphic structures are commonly encountered in these materials, and remarkable photoluminescence has been observed from CuCN and related materials.

Most of the reported CuCN-based networks are produced via hydrothermal or solventothermal synthesis under autogenous pressure. Moreover, some of these compounds are reported as being formed serendipitously, e.g. from Cu(II) salts. Such reactions, even when intentional, tend to suffer from sample size limitations, the need for more specialized equipment (such as pressure-resistant reaction vessels and programmable ovens), and the formation of heterogeneous product mixtures. While CuCN is not soluble in common organic solvents, it is greatly solubilized by aqueous  $\text{CN}^-$ , forming  $[\text{Cu}_x(\text{CN})_y]^{(y-x)-}$  ions under equilibrium conditions [6]. Our group has previously exploited this series of equilibria in order to prepare CuCN networks containing bridging organic ligands in aqueous media containing KCN [1a]–[1c]. To date, only one CuCN-PhPip (1-phenylpiperazine) network has been reported [7]. We use the techniques described herein to uncover the products  $(\text{CuCN})(\text{PhPip})$  (**1**),  $(\text{CuCN})_3(\text{PhPip})_2$  (**2**),  $(\text{CuCN})_5(\text{PhPip})_3$  (**3**) and  $(\text{CuCN})_4(\text{PhPip})$  (**4**) formed in simple binary system with an emphasis on differing CuCN to PhPip ratios.

## Experimental:

### *General:*

CuCN was obtained from Strem Chemicals and used as received. 1-Phenylpiperazine (PhPip) was purchased from Aldrich and was vacuum-distilled prior to use. Water was of standard deionized quality and was degassed with Ar before use. Analyses for C, H, and N were carried out by Atlantic Microlabs, Norcross, GA. Thermogravimetric analyses (TGA) were conducted using a TA Instruments Q500 in the dynamic (variable temp.) mode with a maximum heating rate of 50 °C/min. to 800 °C under 50 mL/min. N<sub>2</sub> flow. Solid state luminescence measurements were made on a Perkin-Elmer LS-55 spectrofluorimeter at ambient temperature using pressed powder samples under quartz glass.

### *General Procedures for Preparation of Complexes.*

*Bulk Synthesis.* CuCN and PhPip (1:1, 3:2, or 4:1 mmol) were combined in 25 mL of 15 mM KCN (aq), or in the case of (CuCN)(PhPip), 25 mL of 40 mM KCN. The PhPip dissolved in the aqueous mixture, while the CuCN remained suspended. Each mixture was placed in a thick-walled screw cap tube under Ar and heated at 80 °C for 48 h, while monitoring changes in luminescence emission under 365 nm irradiation. Occasional shaking of the tube was needed because CuCN and the CuCN-PhPip products are less dense than water. After heating, the solid was collected by filtration and was washed with H<sub>2</sub>O, EtOH and Et<sub>2</sub>O. In all cases a white or nearly white powder was obtained. Analytical data for complexes are given in Table 1.

*Hydrothermal Crystallization.* CuCN (1–5 mmol), KCN (1 mmol), and PhPip (1 mmol) were combined in 5 mL H<sub>2</sub>O, placed in an acid digestion bomb, and flushed with Ar. The mixture was heated for 3 d at 175 °C, cooled to ambient temperature, and collected via filtration. Products, which consisted of mixtures of crystals and powder, were washed with H<sub>2</sub>O, EtOH and Et<sub>2</sub>O.

### *X-ray crystallography.*

Crystals were mounted on glass fibers. All measurements were made using graphite-monochromated Cu K $\alpha$  radiation on a Bruker-AXS three-circle diffractometer, equipped with a SMART Apex II CCD detector. Initial space group determination was based on a matrix consisting of 120 frames. The data were reduced using SAINT+ [8], and empirical absorption correction applied using SADABS [9].

Structures were solved using direct methods. Least-squares refinement for all structures was carried out on  $F^2$ . The non-hydrogen atoms were refined anisotropically. Hydrogen atoms were placed in riding positions and refined isotropically. Structure solution, refinement, and the calculation of derived results were performed using the SHELXTL package of computer programs [10] and Shelxle [11]. Details of the X-ray experiments and crystal data are summarized in Table 2. Selected bond lengths and bond angles are given in Table 3. Racemic twinning noted in **4** was not modeled.

Powder X-ray diffraction (PXRD) data were collected using Rigaku Miniflex diffractometer with Cu K $\alpha$  radiation. Scans were carried out from 3 to 60 degrees 2 theta at 2 deg./min. The data were processed using the MDI-Jade 6.1 software package [12]. Simulated powder patterns from single crystal determinations were generated using the Crystallographica program [13].

## **Results and Discussion:**

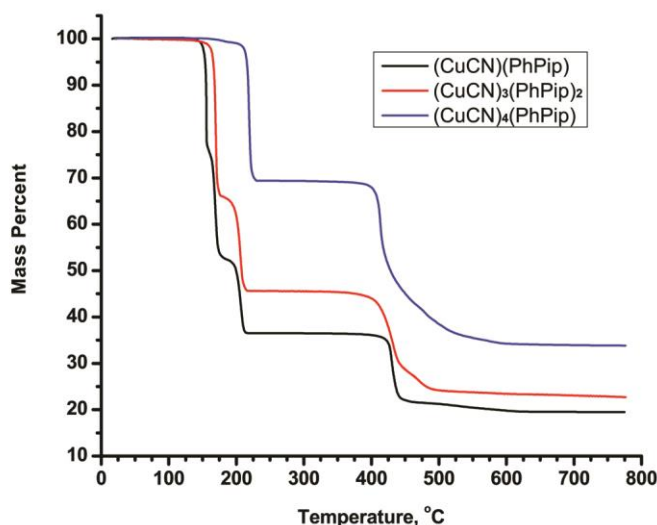
The CuCN-PhPip system was studied using the parallel strategies of bulk and hydrothermal (HT) syntheses. In both approaches KCN was used as a mineralizing agent. A carefully balanced KCN concentration was found to be necessary in the bulk reactions. Use of too little KCN produced CuCN-rich products, while too much KCN gave rise to PhPip-rich products. The 15 mM value proved effective in yielding the desired 3:2 and 4:1 products. However, in order to prepare (CuCN)(PhPip) a higher KCN concentration of 40 mM was required. As noted above, although the HT approach is useful for producing crystals suitable for X-ray diffraction, it tends to yield mixtures of products (as was found in

the current case) and is not convenient for larger scale preparations. Therefore, it is significant that the CuCN-ligand system can be accessed via atmospheric pressure techniques. The use of water as a solvent, in addition to being convenient, green, and inexpensive, confirms the great stability of CuCN toward oxidation in aqueous environments.

Bulk syntheses were attempted using CuCN:PhPip ratios of 1:2, 1:1, 3:2, 5:3, 2:1, 5:2, 3:1, 7:2, 4:1, and 9:2. The 1:1, 3:2, and 4:1 reactions yielded essentially pure products, for which analytical data are given in Table 1; the other reactions resulted in product mixtures. Although we have identified several CuCN-PhPip phases over a variety of experimental conditions, other stable or metastable phases in the CuCN-PhPip system may remain to be synthesized. As it is, at least four stoichiometrically distinct, colorless phases were identified in bulk and HT synthesis: (CuCN)(PhPip) (**1**), (CuCN)<sub>3</sub>(PhPip)<sub>2</sub> (**2**), (CuCN)<sub>5</sub>(PhPip)<sub>3</sub> (**3**), and (CuCN)<sub>4</sub>(PhPip) (**4**). Although the CuCN:PhPip ratio was readily distinguished in the bulk products by using the ligand mass loss observed via thermogravimetric analysis (TGA), this proved to be no guarantee of phase purity. Comparison of products via powder X-ray diffraction (PXRD) was employed to distinguish unique phases from mixtures. Thus, although products roughly corresponding to (CuCN)<sub>5</sub>(PhPip)<sub>2</sub> and (CuCN)<sub>2</sub>(PhPip) could be prepared, their PXRD traces proved to be identical mixtures of compounds **2** and **4**. Phase **3** was identified in HT products; however, all attempts to make this product in bulk reactions were unsuccessful, yielding primarily **2** with **3** as a minor phase. As a result, no elemental analysis was obtained for compound **3**.

A composite TGA of the three unique bulk products is shown in Figure 1. Decomposition of the complexes commences around 175 °C and is complete in all cases by 215 °C, at which point all PhPip has been lost. The residual CuCN decomposes between 400 and 500 °C. Complex **1** shows mass loss plateaus corresponding to formation of complex **2** (theory = 78.5%, actual = 74.4%) and then **4** (theory = 51.7%, actual = 52.3%). Complex **2** shows a plateau reflecting conversion to **4** (theory = 65.8%, actual = 65.8%).

**Figure 1.** TGA results for bulk products **1** (leftmost curve), **2** (center curve), and **4**(rightmost curve).



The least Cu-rich bulk product identified (**1**) is a non-luminescent phase. The bulk product of **1** was relatively easy to prepare, so long as the concentration of KCN was kept fairly high (see above). Crystals having 1:1 stoichiometry were recovered from a complex mixture of crystalline products formed in a 3:1:1 mmol ratio CuCN:PhPip:KCN HT reaction. The same compound was previously reported as being prepared from a solution of Cu(I) in aqueous thiosulfate, and its ambient temperature crystal structure reported by Stocker [7]. For comparison purposes, the structure was redetermined at low temperature in the present work. The new determination produced cell parameters that were slightly contracted, as would be expected at reduced temperature. All atom connectivities were identical in the two structure determinations, with Cu–N, Cu–C, and Cu···Cu bond lengths shortened on average by 1.1% in the new low temperature structure. The PXRD of bulk **1** and the calculated pattern from single crystal structure show a relatively good match (Figure 2). However, the bulk powder shows evidence of preferred orientation causing attenuation of peaks predicted at two theta values of 11, 14, and 22° in the calculated pattern.



Compound **1** (Figure 3) consists of monodentate PhPip ligands, with Cu atoms bonded only through the N<sub>H</sub> position and located in the equatorial piperazine ring positions. Although equatorial positioning of the large Cu atoms might seem to be a fairly likely outcome, equatorial bonding of Cu is commonly seen only for otherwise unsubstituted piperazine N sites [2],[14]. Even N-methylpiperazines usually bond Cu axially at methylated nitrogen atoms, presumably using the more crowded position for the metal atom because it is located at the relatively long bond distance of *ca.* 1.9–2.2 Å. Most known 1:1 CuCN-monodentate ligand compounds consist of 3-coordinate Cu atoms bonded in zigzag CuCN chains [2]. Of note, the structure of **1** does not follow this pattern. Instead, it is akin to only two other compounds: (CuCN)(NH<sub>3</sub>) and (CuCN)(NCMe) [15], *viz*, a 2-D sheet network, wherein the PhPip-Cu units are linked by  $\mu_3$ -C,C,N cyano bridges. The single crystallographically independent cyano unit shows only slight disordering between C1/N1 sites, with the atom position that bridges two Cu sites corresponding to about 81% C (and 19% N) occupancy. The previous determination assigned the bridging atom position as being solely carbon. Copper atoms that share this single cyano atom are held in close proximity, giving rise to a pairwise cuprophilic interaction of 2.5022(5) Å [16]. This value lies well under the van der Waals radius sum of 2.8 Å. The CuCN sheets produced by  $\mu_3$ -C,C,N cyano bridging run parallel to the *b,c* crystallographic plane. The sheets are decorated on both faces with pendent PhPip residues, which show no interactions (e.g.  $\pi$ -stacking) between adjacent sheets. Nevertheless, the saturated piperazine ring centroids are aligned with a long centroid–centroid distance of 4.31 Å.

Figure 2. Experimental (upper trace, red) and calculated PXRD (lower trace, black) comparison for **1** (top), **2** (middle), and **4** (bottom). Minor impurities indicated by \*, see text.

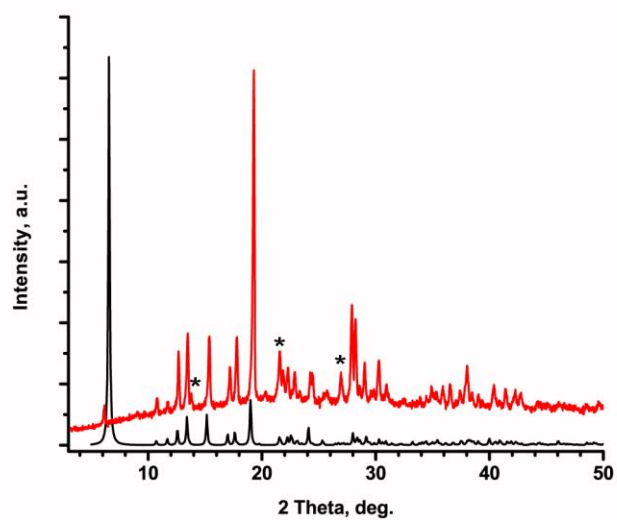
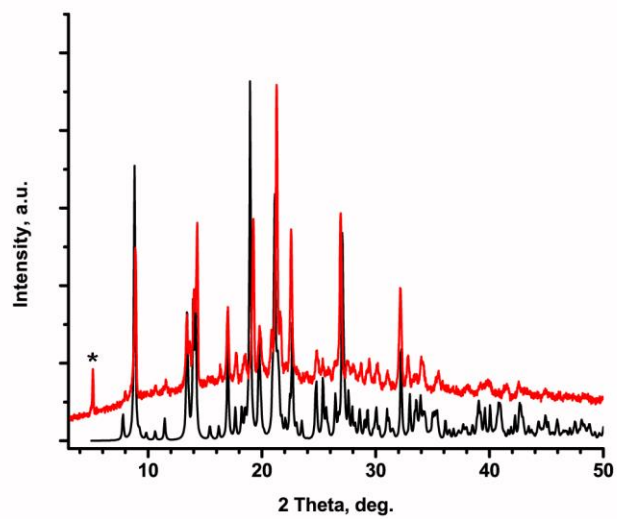
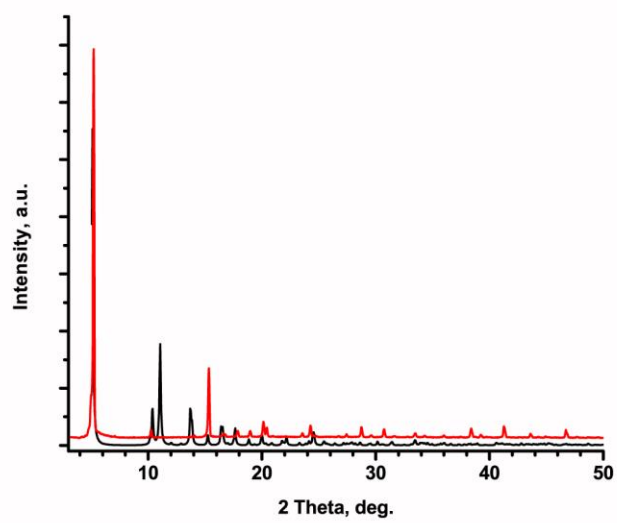
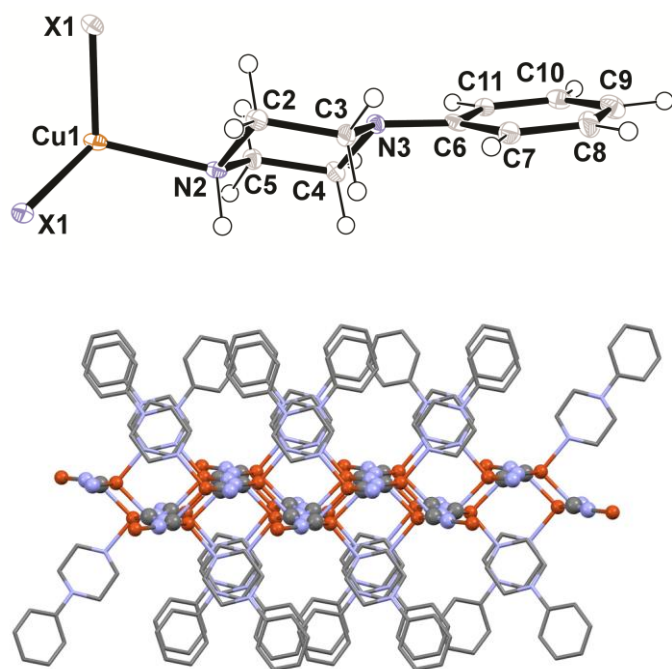


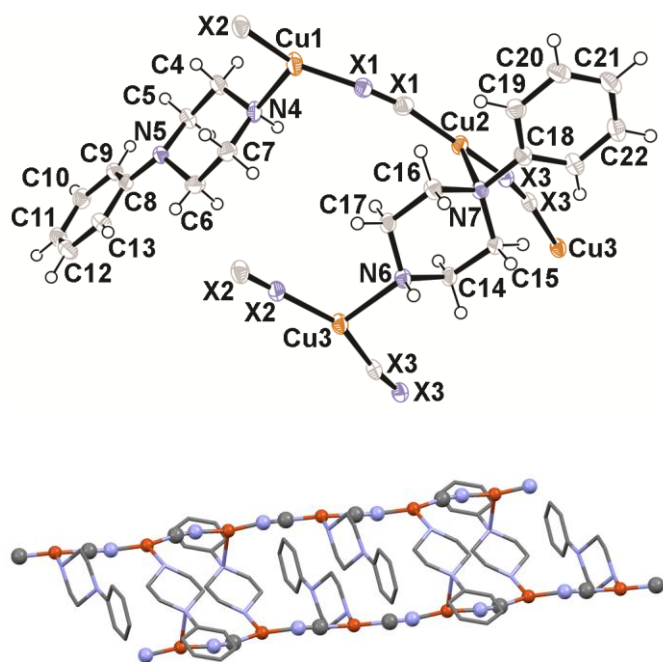
Figure 3. X-ray structure of (CuCN)(PhPip), **1**. Top: Thermal ellipsoid (50%) drawing of repeat unit. Atoms labeled X refer to disorder cyano carbon/nitrogen sites. Bottom: packing diagram viewed along the [001] direction. Cu atoms (orange) and cyano carbon (grey) and nitrogen (blue) atoms shown as ball and stick. Ligands shown as wire frame, with hydrogen atoms omitted.



Compound **2**, ((CuCN)<sub>3</sub>(PhPip)<sub>2</sub>) was prepared both in a bulk tube reaction and as crystals in a 4:1:1 CuCN:PhPip:KCN HT reaction. The PXRD traces showed a good match between the bulk powder and HT crystal (Figure 2). However, a trace of compound **1** was present, as evidenced by the peak near 5° in the PXRD trace indicated with an asterisk (Figure 2). Repeated syntheses using varied amounts of KCN did not remove this impurity. Compound **2** is luminescent, see below. In contrast to **1**, the **2** network structure shows PhPip bridging that serves to knit pairs of CuCN chains into ladders (Figure 4). Only half of the PhPip ligands bridge, resulting in some ladder “rungs” that do not connect the chains, thus producing a ...BBXXBBXX... ligand sequence (B = bridging PhPip, X = pair of non-bridging PhPip). All three independent cyano groups show non-symmetric C/N disorder. Presumably due to the absence of

$\mu_3$ -cyano bridging in **2**, the C/N site occupancy factors were close to random (C1/N1 = 62:38, C2/N2 = 51:49, C3/N3 = 63:37). As is the case with **1**, the pendent PhPip ligands are equatorially  $N_H$  bound. The other independent PhPip bridges pairs of chains via an equatorial  $N_H$  bond and an axial  $N_{Ph}$  bond. The latter bond (Cu2–N7) is rather long (2.3740(17) Å). The ladder chains run roughly along the crystallographic  $a,c$  diagonal, showing no inter-chain interactions.

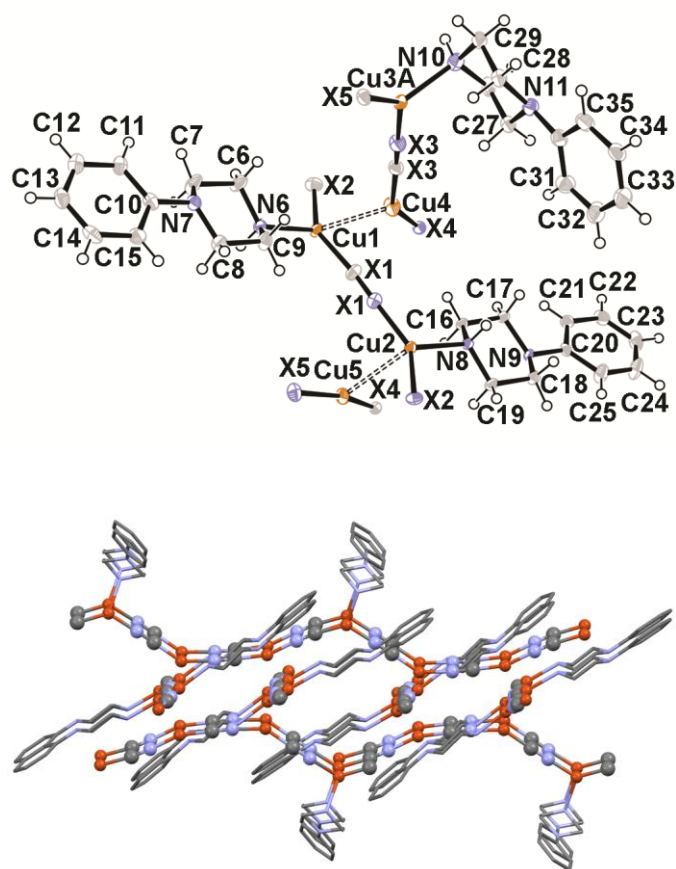
Figure 4. X-ray structure of  $(CuCN)_3(PhPip)_2$ , **2**. Top: Thermal ellipsoid (50%) drawing of repeat unit. Atoms labeled X refer to disorder cyano carbon/nitrogen sites. Bottom: packing diagram viewed along the [111] direction. Cu atoms (orange) and cyano carbon (grey) and nitrogen (blue) atoms shown as ball and stick. Ligands shown as wire frame, with hydrogen atoms omitted.



The only HT network that was not also produced by bulk synthesis procedures was  $(CuCN)_5(PhPip)_3$ , **3**. Crystals of **3** were isolated from a 4:1:1 CuCN:PhPip:KCN HT reaction. The monoclinic crystals were of space group  $P2_1/n$  and contained five independent Cu atoms and five non-symmetrically disordered cyanides (Figure 5). Once again  $\mu_3$ -cyano bridging are absent in **3**. The C/N site occupancy

factors were: C1/N1 = 63:37, C2/N2 = 41:59, C3/N3 = 77:23 and C4/N4 = 67:33. Cu3 is disordered over two positions (Cu3A and Cu3B) which are located 0.925 Å apart, with the major position (Cu3A) being 89% occupied. Two essentially independent 1D chain sub-lattices, (CuCN)(PhPip) and (CuCN)<sub>3</sub>(PhPip), occur in 2:1 ratio. The former is a simple zigzag CuCN polymer of 3-coordinate copper atoms (Cu1 and Cu2) decorated with monodentate PhPip ligands bound through N<sub>H</sub> in equatorial fashion. The resulting chain is roughly planar and lies perpendicular to the *b,c*-plane. Running at an oblique angle to this is the (CuCN)<sub>3</sub>(PhPip) chain which consists of two 2-coordinate centers (Cu4 and Cu5) and 3-coordinate Cu3 axially bound to the N<sub>H</sub> side of a PhPip ligand. Surprisingly, the metal occupies the more crowded axial position in this case, despite the lack of an alkyl substituent at nitrogen. This bond is not particularly long, Cu3A–N10 = 2.107(3) Å. However, it should be noted that the bond lengths and angles associated with Cu3A tend to be outliers with respect to related parameters. This may be connected to the unusual disorder at this site. The two sub-lattices in **3** are associated by Cu<sup>...</sup>Cu pairwise cuprophilic interactions: Cu1<sup>...</sup>Cu4 = 2.5586(10) and Cu(2)<sup>...</sup>Cu(5) = 2.6441(10) Å. Cyano-Cu-cyano bond angles lie between the canonical 3- and 2-coordinate values: 142.5(2), 143.44(18), 130.35(19)° for the formally 3-coordinated Cu1, Cu2, and Cu3, and 144.71(19) and 160.9(2)° for the formally 2-coordinate Cu4 and Cu5. No  $\pi$ -stacking or other intermolecular interactions are in evidence.

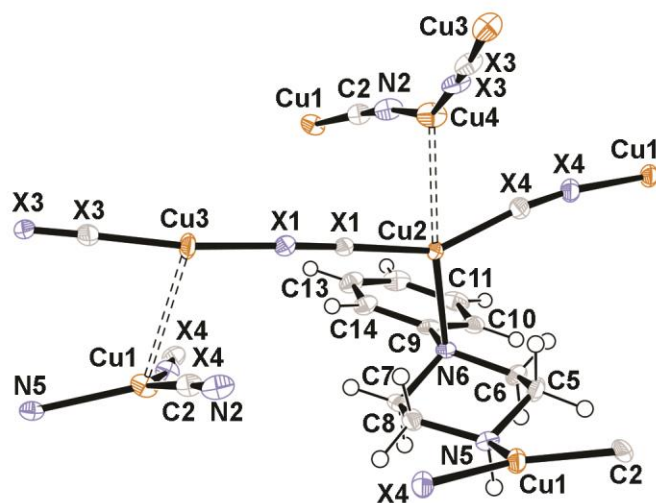
Figure 5. X-ray structure of (CuCN)<sub>5</sub>(PhPip)<sub>3</sub>, **3**. Top: Thermal ellipsoid (50%) drawing of repeat unit. Atoms labeled X refer to disorder cyano carbon/nitrogen sites. Only the higher occupancy position for Cu3 (Cu3A) is shown. Cuprophilic interactions shown as dashed bonds. Bottom: packing diagram viewed along the [010] direction. Cu atoms (orange) and cyano carbon (grey) and nitrogen (blue) atoms shown as ball and stick. Ligands shown as wire frame, with hydrogen atoms and cuprophilic interactions omitted.

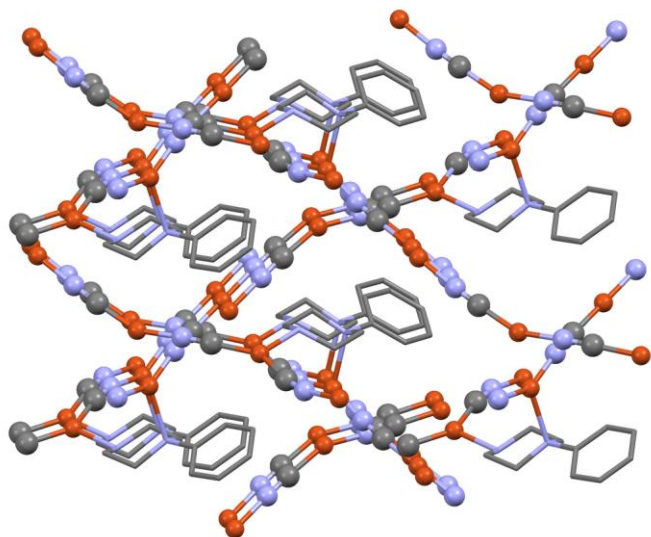


The 4:1 product (**4**), was prepared both in a bulk tube reaction and as crystals in a 4:1:1 CuCN:PhPip:KCN HT reaction. Although the PXRD traces generally showed a good match between the bulk powder and HT-produced crystal (see Figure 2), small peaks at two theta values of 14, 21, and 27° suggest the presence of a small impurity of complex **2**. The compound showed no luminescence activity. Although **4** crystallized in a Sohncke space group ( $P2_1$ ), the Flack parameter was ambiguous, 0.33(3), suggesting racemic twinning. The structure of this most CuCN-rich PhPip product consists of CuCN chains running in two perpendicular directions (Figure 6). The chains are comprised of two 2-coordinate Cu centers bound only to cyanide and two 3-coordinate Cu centers that also coordinate PhPip bridges. The single crystallographically independent PhPip bridges adjacent CuCN chains forming 2-D sheets. The PhPip ligands all lie on a single face of the sheet. Pairwise cuprophilic interactions ( $\text{Cu1}\cdots\text{Cu3} = 2.7633(7)$ ,  $\text{Cu2}\cdots\text{Cu4} = 2.6173(7)$  Å) produce de facto links between the two identical, orthogonally-oriented sheets,

producing a 3-D arrangement. The equatorial  $N_H$  and axial  $N_{Ph}$  bonds to copper are somewhat different in length: 2.123(3), 2.195(3) Å respectively. Three of the four independent cyano groups are non-symmetrically C/N disordered. None of the cyano ligands show  $\mu_3$  behavior. While C2/N2 is fully ordered, C/N site occupancy factors for the other cyanide ligands are C1/N1 = 78:22, C3/N3 = 54:46, and C4/N4 = 58:42. No  $\pi$ -stacking or other intermolecular interactions are in evidence.

Figure 6. X-ray structure of  $(CuCN)_4(PhPip)$ , **4**. Top: Thermal ellipsoid (50%) drawing of repeat unit. Atoms labeled X refer to disorder cyano carbon/nitrogen sites. Cuprophilic interactions shown as dashed bonds. Bottom: packing diagram viewed along the [100] direction. Cu atoms (orange) and cyano carbon (grey) and nitrogen (blue) atoms shown as ball and stick. Ligands shown as wire frame, with hydrogen atoms and cuprophilic interactions omitted.

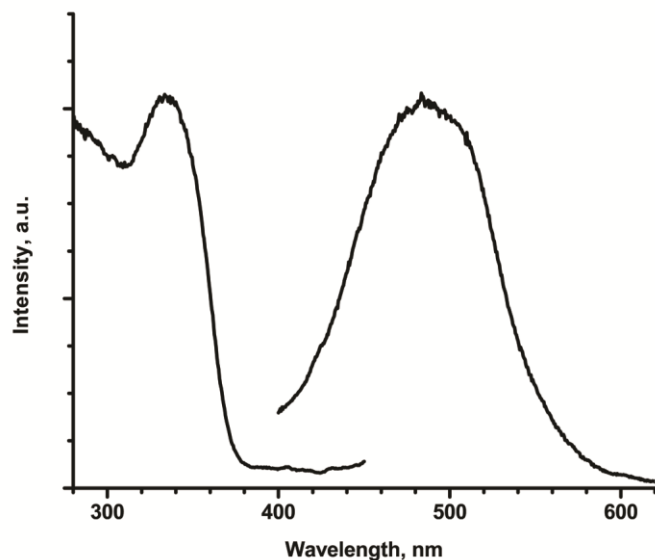




Of the four CuCN-PhPip compounds described herein, **2** is the only one that shows measurable photoluminescence, exhibiting moderately intense blue-green emission with  $\lambda_{\text{max}}$  for excitation and emission = 334 and 484 nm, respectively (Figure 7). Compound **2** is also the only one of the four structures lacking cuprophilic interactions. While this observation might suggest that Cu $\cdots$ Cu interactions necessarily cause luminescence quenching, numerous CuCN-amine networks both with and without cuprophilic interactions show luminescence [1c]. The photoluminescent behavior in CuCN networks is best understood as being associated with a metal-to-ligand charge transfer (MLCT) transition between Cu d and cyano  $\pi^*$  orbitals [17]. Copper(I) cyanide MLCT results in emission at relatively short wavelengths (including in the present case) due to very limited structural alteration during transition from the ground to excited state. Quenching of photoluminescence in CuCN-amine compounds is likely related to vibrational relaxation through the solid network. This relaxation in **1** could occur through the 2-D sheets. In **3** and **4** the cuprophilic interactions serve to create higher dimensional networks, allowing for relaxation. Thus, we suggest that it is not the Cu $\cdots$ Cu interactions themselves, but their network-forming action that removes luminescence behavior in the cases of **3** and **4**.



Figure 7. Luminescence spectrum of  $(\text{CuCN})_3(\text{PhPip})_2$ , **2**. Left hand trace: excitation scan (emission monitored at 484 nm), right hand trace: emission scan (excitation at 334 nm).



## Conclusions:

We have shown that at least three different PhPip-linked CuCN networks, with CuCN:PhPip ratios of 1:1, 3:2, and 4:1, may be synthesized in bulk from aqueous KCN solutions through stoichiometric control. Another phase with 5:3 stoichiometry is accessible through hydrothermal reaction.  $(\text{CuCN})(\text{PhPip})$  is a 2-D sheet consisting of  $\mu_3$ -cyano bridged Cu atoms with monodentate PhPip.  $(\text{CuCN})_3(\text{PhPip})_2$  is a 1-D ladder with both monodentate and bridging PhPip ligands.  $(\text{CuCN})_5(\text{PhPip})_3$  consists of the 1D chain sublattices  $(\text{CuCN})(\text{PhPip})$  and  $(\text{CuCN})_3(\text{PhPip})$ , featuring only monodentate PhPip.  $(\text{CuCN})_4(\text{PhPip})$  is formed from two identical  $\mu$ -PhPip 2D sheets. Further,  $(\text{CuCN})_3(\text{PhPip})_2$  displays photoluminescence.

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**Table 1.** Bulk Synthesis and Analytical Results.

Product	% Yield	Color	% CuCN (TGA) <sup>a</sup>	% C <sup>a</sup>	% H <sup>a</sup>	% N <sup>a</sup>
(CuCN)(PhPip), <b>1</b>	70.5	white	37.3 (35.6)	51.99 (52.47)	5.59 (5.60)	16.69 (16.69)
(CuCN) <sub>3</sub> (PhPip) <sub>2</sub> , <b>2</b>	82.1	cream	45.2 (45.3)	46.31 (46.57)	4.72 (4.76)	16.48 (16.53)
(CuCN) <sub>4</sub> (PhPip), <b>4</b>	60.3	cream	69.4 (68.8)	32.40 (32.31)	2.55 (2.71)	16.09 (16.15)

<sup>a</sup>Calculated values in parenthesis.

**Table 2.** Crystal and Structure Refinement Data.

	(CuCN)(PhPip) ( <b>1</b> )	(CuCN) <sub>3</sub> (PhPip) <sub>2</sub> ( <b>2</b> )	(CuCN) <sub>5</sub> (PhPip) <sub>3</sub> ( <b>3</b> )	(CuCN) <sub>4</sub> (PhPip) ( <b>4</b> )
CCDC deposit no.	952007	952008	952009	952010
color and habit	colorless prism	colorless plate	colorless prism	colorless plate
size, mm	0.27 × 0.07 × 0.05	0.25 × 0.23 × 0.02	0.17 × 0.09 × 0.07	0.29 × 0.24 × 0.08
formula	C <sub>11</sub> H <sub>14</sub> Cu <sub>1</sub> N <sub>3</sub>	C <sub>23</sub> H <sub>28</sub> Cu <sub>3</sub> N <sub>7</sub>	C <sub>35</sub> H <sub>42</sub> Cu <sub>5</sub> N <sub>11</sub>	C <sub>14</sub> H <sub>14</sub> Cu <sub>4</sub> N <sub>6</sub>
formula weight	251.79	593.14	934.50	520.47
space group	<i>P</i> 2 <sub>1</sub> / <i>c</i>	<i>P</i> -1	<i>P</i> 2 <sub>1</sub> / <i>n</i>	<i>P</i> 2 <sub>1</sub>
<i>a</i> , Å	17.6123(3)	9.93710(10)	15.9018(2)	7.8460(2)
<i>b</i> , Å	6.89480(10)	10.6359(2)	9.38850(10)	13.4773(3)
<i>c</i> , Å	8.6154(2)	12.1230(2)	26.1864(3)	8.5527(2)
α, deg	90	105.7110(10)	90	90
β, deg	96.1460(10)	100.6110(10)	104.5110(10)	105.1820(10)
γ, deg	90	97.7230(10)	90	90
volume, Å <sup>3</sup>	1040.18(3)	1189.11(3)	3784.76(8)	872.82(4)
<i>Z</i>	4	2	4	2
ρ <sub>calc</sub> , g cm <sup>-3</sup>	1.608	1.657	1.640	1.980
<i>F</i> <sub>000</sub>	520	604	1896	512
μ(Cu Kα), mm <sup>-1</sup>	2.687	3.315	3.427	5.542
radiation	CuKα (λ= 1.54178 Å)	CuKα (λ= 1.54178 Å)	CuKα (λ= 1.54178 Å)	CuKα (λ= 1.54178 Å)
temperature, K	100	100	100	100
residuals: <sup>a</sup> <i>R</i> ; <i>R</i> <sub>w</sub>	0.0226, 0.0600	0.0300, 0.0806	0.0372, 0.0936	0.0184, 0.0476
goodness of fit	1.049	1.068	1.100	1.018
Flack parameter	–	–	–	0.33(3)

<sup>a</sup>*R* =  $R_1 = \sum ||F_o| - |F_c|| / \sum |F_o|$  for observed data only. *R*<sub>w</sub> =  $wR_2 = \{\sum [w(F_o^2 - F_c^2)^2] / \sum [w(F_o^2)^2]\}^{1/2}$  for all data.

**Table 3.** Selected bond lengths (Å) and angles (°).<sup>a</sup>

(CuCN)(PhPip), <b>1</b>			
Cu-X	1.9393(15), 1.9994(16)	Cu-X-X	128.88(13), <sup>b</sup> 159.90(14), <sup>b</sup> 172.80(14)
X-X	1.154(2)	X-Cu-X	106.88(6), 109.11(5), 120.76(6)
Cu-N	2.1267(14)	X-Cu-N	95.86(6), 104.57(6), 116.70(6)
Cu1-Cu1'	2.5022(5)		
(CuCN) <sub>3</sub> (PhPip) <sub>2</sub> , <b>2</b>			
Cu-X	1.881(2), 1.890(2), 1.8512(19), 1.854(2), 1.876(2), 1.885(2)	Cu-X-X	167.82(19), 168.30(19), 170.97(18), 170.97(18), 171.26(18), 173.80(19)
X-X	1.161(3), 1.163(3), 1.164(3)	X-Cu-X	145.13(9), 149.55(9), 160.12(9) <sup>c</sup>
Cu-N	2.1539(18), 2.1608(18), 2.3740(17) <sup>c,d</sup>	X-Cu-N	97.87(7), <sup>c</sup> 101.15(7), <sup>c</sup> 103.72(8), 104.02(8), 105.87(8), 107.84(8)
(CuCN) <sub>5</sub> (PhPip) <sub>3</sub> , <b>3</b>			
Cu-X	1.854(3), <sup>e</sup> 1.854(3), <sup>e</sup> 1.874(3), <sup>d,f</sup> 1.879(3), <sup>e</sup> 1.879(3), <sup>e</sup> 1.883(3), 1.884(3), 1.889(3), 1.898(3), 1.913(3) <sup>d,f</sup>	Cu-X-X	172.2(3), <sup>d,f</sup> 174.9(3), <sup>e</sup> 175.1(3), 175.2(3), <sup>e</sup> 175.5(3), 175.7(3), 177.2(3), 178.3(3), <sup>d,f</sup> 178.3(3), <sup>e</sup> 178.5(3) <sup>e</sup>
X-X	1.150(4), 1.153(4), 1.154(4), 1.155(4), 1.156(4)	X-Cu-X	130.26(13), <sup>d,f</sup> 142.38(13), 143.41(12), 144.87(13), <sup>e</sup> 161.02(13) <sup>e</sup>
Cu-N	2.096(2), 2.093(2), 2.107(3) <sup>d,f</sup>	X-Cu-N	103.66(12), <sup>d,f</sup> 106.98(11), 107.54(11), 109.04(10), 109.68(11), 126.07(12) <sup>d,f</sup>
Cu1-Cu4	2.5577(7)		
(CuCN) <sub>4</sub> (PhPip), <b>4</b>			
Cu-X	1.847(3), 1.849(3), 1.857(3), 1.857(3), 1.871(3), 1.894(3), 1.875(4), 1.877(3)	Cu-X-X	167.4(3), <sup>c,d</sup> 170.0(3), 170.4(3), <sup>e</sup> 175.2(3), <sup>c,d</sup> 176.2(3), <sup>e</sup> 177.0(3), <sup>e</sup> 177.8(3), 178.0(3) <sup>e</sup>
X-X	1.151(5), 1.152(5), 1.153(5), 1.156(5)	X-Cu-X	140.04(16), 149.72(14), <sup>c,d</sup> 155.15(14), <sup>e</sup> 172.18(14) <sup>e</sup>

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Cu-N	2.123(3), 2.195(3) <sup>c,d</sup>	X-Cu-N	102.69(13), <sup>c,d</sup> 106.95(13), 107.47(13), <sup>c,d</sup> 113.02(15)
Cu-Cu	2.7633(7), 2.6173(7)		

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<sup>a</sup>X indicates cyanide C/N, N indicates L ligand. All Cu atoms 3-coordinate, bonded to N<sub>H</sub>, and equatorial to piperazine ring, except as noted. <sup>b</sup>Central X atom bridges two Cu atoms. <sup>c</sup>N<sub>Ph</sub>. <sup>d</sup>Cu axial to piperazine ring. <sup>e</sup>2-Coordinate Cu atom. <sup>f</sup>Cu3 atom disordered over two positions; major Cu3A position used.